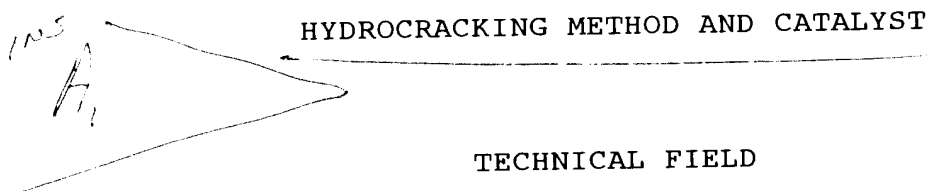


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## DESCRIPTION



The present invention relates to a hydrocracking method for cracking feed oil, such as petroleum oil, and a hydrocracking catalyst used in this method, and in particular, the present invention relates to pre-treatment that is performed before cracking the feed oil and hydrocracking catalyst that has been pre-treated.

## BACKGROUND OF ART

Attention has recently been focused on hydrocracking as a method of cracking heavy oils to obtain light oils. This is because not only gasoline, but also middle distillate products, such as kerosene and gas oil, etc., are obtained by hydrocracking and their yields can be changed by changing operating conditions, and because quality of the product oil is the high quality that is suitable for the environment.

Two-stage hydrocracking is one known method of hydrocracking. Two-stage hydrocracking is conducted using, for instance, a two-stage hydrocracking system such as shown in Fig. 4. By means of this method, hydrogen and feed oil are fed to

first-stage reactor (or hydrorefining area) 41 loaded with hydrocracking catalyst and the feed oil is hydrocracked here. Hydrorefining is simultaneously performed with hydrocracking of the feed oil to pre-remove the nitrogen compounds, which are poisons of the hydrocracking catalyst loaded in second reactor 45. The outlet oil emitted from first-stage reactor 41 is sent to distillation tower 43 and the light fraction is distilled off here, while some of the heavy oil that remains is recycled to second-stage reactor 45. The nitrogen content of the heavy oil that is recycled to the hydrocracking catalyst in second-stage reactor 45 is less than 100 ppm. The product oil that has been hydrocracked at second-stage reactor 45 is again sent to distillation column 43 together with the outlet oil of first-stage reactor 41.

The hydrocracking catalyst used by second-stage reactor 45 of two-stage hydrocracking is usually pre-sulfided in the gas phase by introducing sulfiding agent to the hydrogen gas prior to starting the hydrocracking operation. Therefore, (the acid sites on) the catalyst loaded in second-stage reactor 45 will not be poisoned by nitrogen while pre-sulfiding is being performed.

Nevertheless, although the catalyst loaded in second-stage reactor 45 initially has high activity, once the hydrocracking operation is started, it becomes poisoned by the nitrogen contained in the nitrogen compound in the recycle oil and

deactivation quickly occurs. Moreover, once the large volumes of nitrogen compounds, such as the polycyclic aromatics and the compounds whose side chain is attached to carbazole in the recycle oil are adsorbed on the acid sites on the catalyst, they cause coke deactivation and as a result, the active sites around the acid sites that have adsorbed nitrogen compounds are poisoned, leading to a reduction in activity following initial deactivation.

Therefore, there is technology for preventing this deactivation of hydrocracking catalysts whereby the catalyst is pre-treated with ammonia either before the hydrocracking operation or at the beginning of hydrocracking. This technology is disclosed in US Patents No. 3,117,075, No. 3,778,365, No. 5,141,909, and No. 5,366,615. Moreover, technology is also known whereby a nitrogen compound, such as a basic nitrogen compound, and ammonia are added to hydrorefined recycle oil to treat the catalyst during the hydrocracking operation. This technology is disclosed in US Patents No. 3,213,013, No. 3,404,085, No. 3,505,208, and No. 3,816,296.

Nevertheless, according to the research of the inventors, it is difficult to retain catalyst deactivation inhibiting effect for a long enough period of time by the method whereby catalyst is treated using ammonia either before the hydrocracking operation or at the beginning of the operation. Moreover,

because hydrotreating readily occurs with the treatment using a nitrogen compound having a low boiling point, such as butyl amine, etc., disclosed in US Patent No. 3,213,013, catalyst deactivation inhibiting effect is not retained for a long enough period of time. Moreover, it is necessary to add relatively large volumes of conventional additives, with the amount of nitrogen compound added per feed oil being 5 to 200 ppm (nitrogen concentration).

#### DISCLOSURE OF THE INVENTION

The present invention solves the above-mentioned problems of background art, its object being to provide a hydrocracking method and a hydrocracking catalyst used by this method with which the initial deactivation rate of the hydrocracking catalyst is slowed and the middle distillate yield is improved and further, activity following initial deactivation is improved.

In accordance with the first aspect of the present invention, a method of hydrocracking hydrocarbon oils is provided, which comprises the steps of:

pre-contacting a hydrocracking catalyst with an organic nitrogen compound; and

contacting a feed oil substantially comprised of hydrocarbon oils and hydrogen with the hydrocracking catalyst that has been

contacted with the organic nitrogen compound in order to obtain a hydrocarbon oil with a lower boiling point than the feed oil;

the organic nitrogen compound being an organic nitrogen compound having a boiling point that is lower than a 50% distillation temperature of the feed oil and that is higher than 200°C.

The inventors discovered that covering (poisoning) the acid points of a hydrocracking catalyst with an organic nitrogen compound having appropriate adsorbing power and appropriate molecular size is effective for i) slowing the initial deactivation rate of the hydrocracking catalyst, ii) improving the middle distillate yield, and iii) improving activity following initial deactivation. The organic nitrogen compound used by the present invention is an organic nitrogen compound a boiling point that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C. It has a boiling point lower than the 50% distillation temperature of the feed oil because organic nitrogen compounds having too large molecular size should be removed. An organic nitrogen compound with a boiling point that is lower than (50% distillation temperature (°C))  $\times 0.9$  is further preferred. Moreover, the organic compound must have a boiling point higher than 200°C for the following reason. That is, it appears that an organic nitrogen compound with a boiling point of 200°C or lower cannot sufficiently cover

(be adsorbed on) the acid sites on a catalyst that is readily decomposed by hydrocracking for long periods of time. Moreover, if the organic nitrogen compound has a boiling point of 200°C or lower, molecular size is also relatively small and it cannot sufficiently cover the acid sites, and the compound is likely to relatively easily desorbed from the acid sites.

According to the method of the present invention, the above-mentioned organic nitrogen compound is contacted by hydrocracking catalyst prior to starting the hydrocracking operation. In contrast to the methods described in the above-mentioned published document, the organic nitrogen compound specified by the present invention is contacted with catalyst prior to the hydrocracking operation, not during the operation. Thus, a specific nitrogen compound is pre-contacted with catalyst prior to the hydrocracking operation so that the acid sites of the catalyst are covered by the organic nitrogen compound and therefore, even a very small amount of organic nitrogen compound is effective for long-term prevention of catalyst deactivation. For instance, the amount of organic nitrogen absorbed on a catalyst can be kept at 0.01% to 1% in terms of nitrogen weight per catalyst.

The method of the present invention further may comprise the step of sulfiding the above-mentioned hydrogenation catalyst and it is preferred that treatment whereby the above-mentioned

organic nitrogen compound is contacted with hydrocracking catalyst be performed simultaneously with the sulfiding treatment. When tert-butyl amine (b.p.: 44°C), which has been conventionally used, is mixed with gas oil in which carbon sulfide ( $\text{CS}_2$ ) for sulfiding treatment has been dissolved, a white precipitate forms, but a white precipitate does not form when the organic nitrogen compound having a boiling point of 200°C or higher in accordance with the present invention, such as tributyl amine (b.p.: 217°C), is mixed with gas oil. Therefore, pretreatment with the organic nitrogen compound is simultaneously performed with sulfiding treatment and as a result, the process can be simplified and the time needed for the entire process can be curtailed.

In accordance with the second aspect of the present invention, a method of hydrocracking hydrocarbon oils derived from petroleum is provided, which comprises the steps of:

contacting a petroleum fraction containing an organic nitrogen compound and having a 95% distillation temperature that is lower than the 50% distillation temperature of a feed oil substantially comprised of hydrocarbon oils and that is higher than 200°C with a hydrocracking catalyst; and

contacting the feed oil and hydrogen with the hydrocracking catalyst that has been contacted with the petroleum fraction in

order to obtain a hydrocarbon oil with a boiling point lower than the feed oil.

As with the first method, according to the hydrocracking method of this embodiment, it is possible to i) slow the initial deactivation rate of the hydrocracking catalyst, ii) improve the middle distillate yield, and iii) improve activity following initial deactivation. The petroleum fraction with a 95% distillation temperature that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C includes, for instance, gas oil and kerosene. The boiling point of gas oil is 220°C to 380°C and the boiling point of kerosene is 140°C to 250°C. Organic nitrogen compounds, such as aniline, pyridine, quinoline, indole, carbazole, and their derivatives, etc., are contained in the petroleum fraction used in the present invention. It appears that because these organic nitrogen compounds are contained in the petroleum fraction with a 95% distillation temperature higher than 200°C, the acid sites on the catalyst can be protected for a long period of time during the hydrocracking process. In order to perform the method of this embodiment, the hydrocracking catalyst should be pre-treated by being brought into contact with, for instance, gas oil or kerosene. The gas oil can be straight run gas oil, coker gas oil, gas oil obtained from desulfurization of vacuum gas oil,



their mixtures, gas oil obtained by hydrotreating these examples, etc.

In accordance with the third aspect of the present invention, a hydrocracking catalyst, which is used for hydrocracking a feed oil derived from petroleum by contacting the feed oil and hydrogen with the hydrocracking catalyst to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil, is provided. The hydrocracking catalyst comprises:

a carrier made from a porous refractory oxide;

a hydrogenation active metal component; and

an organic nitrogen compound with a boiling point that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C; the content of the organic nitrogen compound being not less than 0.01 wt% by nitrogen weight per the hydrogenation catalyst.

It is preferred that the hydrocracking catalyst does not contain organic compound having a boiling point exceeding the 50% distillation temperature of the feed oil because organic nitrogen compounds having too large molecular size should be removed.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the process flow of a hydrocracking system capable of performing the hydrocracking method of the present invention.

Fig. 2 shows the process flow of a different hydrocracking system capable of performing the hydrocracking method of the present invention.

Fig. 3 shows the process flow of a different hydrocracking system capable of performing the hydrocracking method of the present invention that is equipped with a recycle system.

Fig. 4 shows the process flow of a two-stage hydrocracking system capable of performing the hydrocracking method of the present invention.

Fig. 5 shows the process flow of a series flow-type hydrocracking system capable of performing the hydrocracking method of the present invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The feed oil that serves as the starting material of the hydrocracking process of the present invention is usually feed oil with a 10% distillation temperature of 200°C or higher, preferably a 10% distillation temperature of 300°C or higher. There are no special restrictions to the feed oil, but feed oil derived from crude oil, coal liquefaction oil, oil shell, oil sand, etc., and Fischer-Tropsch synthetic oil, etc., are preferably used. The hydrocracking method and catalyst of the present invention is particularly effective for feed oil that has been hydrotreated to a nitrogen content of 100 ppm or less,

preferably 10 ppm or less, particularly 2 ppm or less. Such hydrorefined feed oil is, for instance, feed oil that has passed through the first stage of hydrocracking of two-stage hydrocracking.

Typical examples of the flow process of hydrocracking systems capable of using the hydrocracking method of the present invention are shown in Figs. 1 to 5. The system shown in Fig. 1 uses a reactor in only 1 stage, but the system in Fig. 2 uses reactors in two stages. The systems in Figs. 3 to 5 each have a recycle path from the distillation tower to the reactor. By means of the system in Fig. 4, once hydrocracking of feed oil has been performed by first-stage reactor 41, the oil is sent to distillation tower 43 and the light oil is recovered, while the remaining heavy oil is sent to second-stage reactor 45. After hydrocracking in second-stage reactor 45, the oil is again sent to distillation tower 43. By means of the system shown in Fig. 5, the first-stage reactor, second-stage reactor, and distillation tower are connected in this order and the heavy oil from the distillation tower is recycled to the second-stage reactor. By means of the systems in Figs. 4 and 5, hydrorefining is performed at once with the first-stage reactor and therefore, these systems are suitable for the hydrocracking method of the present invention. Consequently, the hydrocracking catalyst of the present invention is suitable as the catalyst used by the

second-stage reactor of a two-stage or a multi-stage hydrocracking system, such as shown in Figs. 4 and 5.

Nevertheless, the present invention can also be used for hydrocracking by the process flow in Figs. 1 and 2 using fraction that has been hydrorefined at least once as the starting material.

The hydrocracking of the present invention is a process whereby fractions corresponding to kerosene, gas oil, etc., that are lighter fractions than the feed oil are obtained, and the actual catalyst and operating conditions are selected so that fractions with a boiling point of 300°C or lower, particularly 125°C to 300°C, are obtained at a yield of 50% or higher.

The catalyst that is used is formed by supporting a hydrogenation active metal component, etc., on a carrier consisting of porous refractory material. Alumina, boria-alumina, silica-alumina, silica-titania, silica-zirconia, silica-magnesia, silica-alumina-titania, silica-alumina-zirconia, and their mixtures, as well as compound oxides of zeolite mixed with these are preferred as the carrier. In addition, a metal from Group 6, Group 9 or Group 10 of the Periodic Table is preferably used for the hydrogenation active metal component and actually, tungsten, molybdenum, nickel, cobalt, etc., can be used. Combination of tungsten or molybdenum and nickel or cobalt is particularly preferred. It is preferred that the total weight of

metal per catalyst weight of these metal components that is used be 1 to 35 wt%, particularly 5 to 30 wt%.

The organic nitrogen compound used in the present invention is an organic nitrogen compound whose boiling point is lower than the 50% distillation temperature of the starting material, particularly lower than  $(50\% \text{ distillation temperature } (^{\circ}\text{C})) \times (0.9)$  and exceeds  $200^{\circ}\text{C}$ , or a nitrogen compound contained in petroleum fractions whose 95% distillation temperature is lower than the 50% distillation temperature of the feed oil, particularly lower than  $(50\% \text{ distillation temperature } (^{\circ}\text{C})) \times (0.9)$ , and exceeds  $200^{\circ}\text{C}$ . Organic nitrogen compounds such as amines, pyridine, quinoline, indole, carbazole, etc., can be given as actual examples. Furthermore, derivatives of these organic nitrogen compounds and derivatives of other organic nitrogen compounds whose boiling point exceed  $200^{\circ}\text{C}$ , such as aniline derivatives, can be used.

The amount of organic nitrogen compound contained in the hydrogenation catalyst of the present invention is 0.01% or higher, preferably 0.1% to 1% in particular, in terms of the nitrogen weight. Because the organic nitrogen compound used by the present invention has the above-mentioned boiling point range and is contacted with catalyst before the hydrocracking process, the amount added can be very little when compared to conventional nitrogen compound additives.

The organic nitrogen compound can be added during catalyst production, but it is also possible to contact the nitrogen compound with the catalyst after the catalyst is loaded into the reactor so that the catalyst will contain the nitrogen compound. The organic nitrogen compound can be efficiently contacted with the catalyst after it has been loaded in the reactor by a process of bringing catalyst and organic nitrogen compound into contact prior to hydrocracking, for instance, during pre-sulfiding treatment. Furthermore, it is also possible to contact the organic nitrogen compound with the catalyst prior to the hydrocracking process, and thereafter to add nitrogen compound to the reactor during the hydrocracking process. In this case, the nitrogen compound can be mixed in the feed oil that serves as the starting material of the hydrocracking reaction, or it can be mixed in gas, such as hydrogen, etc., that will be introduced to the reactor. The nitrogen compound added to the hydrocracking reaction acts as a catalyst deactivation inhibitor, and in addition to the above-mentioned organic nitrogen compounds, can be ammonia or another nitrogen compound.

The organic nitrogen compound used in the present invention can be used as a compound alone, but it is simpler to use the organic nitrogen compound contained in the petroleum fraction. Actually, kerosene, gas oils, etc., that are ordinarily marketed can be used, and it is preferred that one whose nitrogen content

has been reduced to 2 to 200 ppm, preferably 2 to 100 ppm, particularly 10 to 100 ppm by hydrorefining be used. It is possible to bring the catalyst into contact with a solution of sulfiding agent dissolved in a solvent such as kerosene, gas oil, etc., and perform sulfiding so that organic nitrogen compound will be contained in the catalyst as a result of the sulfiding. Carbon disulfide, dimethyl sulfide, dimethyl disulfide, etc., can be used as the sulfiding agent.

#### EXAMPLES

Examples of contacting catalyst loaded in second-stage reactor 45 with an organic nitrogen compound when kerosene or gas oil fraction is to be produced by two-stage hydrocracking using the system shown in Fig. 4 with vacuum gas oil as the feed oil are described below.

##### Example 1

The feed oil fed to first-stage reactor 41 of the two-stage hydrocracking system is petroleum fraction with a boiling point range of 300 to 540°C and a nitrogen concentration 800 ppm. The product oil obtained from first-stage reactor 41 is distilled by distillation tower 43 and the fraction from the bottom of distillation tower 43 becomes the feed oil (recycle oil) of second-stage reactor 45. The product oil of second-stage reactor

45 and the product oil of first-stage reactor 41 are mixed and fed to distillation tower 43. The feed oil of this second-stage reactor 45 has a boiling point range of 290°C ~ 540°C and a nitrogen concentration of 1 ppm. The catalyst was hydrocracking catalyst comprising a nickel and a tungsten metal component on a silica-alumina carrier for both the first-stage and the second-stage reactor.

Prior to hydrocracking, pre-sulfiding of the catalyst loaded in second-stage reactor 45 was performed by passing gas oil (boiling point of 250 to 360°C) to which 1 wt% carbon disulfide had been added as the sulfiding agent through second-stage reactor 45. The sulfur concentration of the gas oil was 400 ppm and the nitrogen concentration was 50 ppm. Of these, it was shown that the gas oil contained 17 ppm acidic nitrogen compounds which are indole and carbazole derivatives and 16 ppm basic nitrogen compounds which are aniline, pyridine, and quinoline derivatives.

The time for which the gas oil was passed through the reactor during pre-sulfiding was adjusted so that the concentration of nitrogen adsorbed on the catalyst in second-stage reactor 45 would be 0.4% (nitrogen weight / loaded catalyst (fresh catalyst) weight).

Once pre-sulfiding was completed, operation of the system in Fig. 4 was switched to a two-stage hydrocracking operation and



hydrocracking was started. The hydrocracking operation lasted for 620 hours. It was found that the initial deactivation rate is 0.5°C/month or less. It was necessary to bring the reaction temperature of second-stage reactor 45 to 377°C in order to keep the conversion of fractions of 290°C or higher at 95 vol% after initial deactivation. The yield of middle distillates (130 to 290°C) was 66% (middle distillate weight/feed oil weight).

#### Example 2

Hydrocracking without recycling was performed using a system equipped with a one-stage reactor as shown in Fig. 1 with petroleum fraction with a nitrogen concentration of 1 ppm and a boiling point range of 290 to 540°C serving as the starting materials. The catalyst was hydrocracking catalyst comprising nickel and tungsten metal components supported on a silica-alumina carrier.

Pre-sulfiding of the catalyst was performed prior to hydrocracking by passing gas oil (boiling point range of 250°C to 360°C) to which 1 wt% carbon disulfide had been added as sulfiding agent through the reactor loaded with catalyst. The sulfur concentration of the gas oil was 400 ppm and the nitrogen concentration was 50 ppm. The time for which the gas oil was passed through the reactor was adjusted during sulfiding so that the nitrogen concentration adsorbed on the catalyst in the

reactor would be 0.4 % (nitrogen weight/loaded catalyst (fresh catalyst) weight).

When hydrocracking was started at a constant reaction temperature of 380°C once pre-sulfiding was completed, the conversion of fraction of 290°C or higher was 56% and the yield of middle distillates (130 to 290°C) was 38%.

#### Example 3

Other than the fact that 1% zeolite added to the carrier was used as the catalyst in the second-stage reactor, pre-sulfiding treatment of the catalyst and hydrocracking were performed under the same conditions as in Example 1. The reaction temperature of the second-stage reactor with which the conversion of fractions of 290°C or higher is 95 vol% was 377°C. The yield of middle distillates (130 to 290°C) was 64%.

#### Example 4

Tert-butyl amine (catalyst deactivation inhibitor) was mixed at 0.3 ppm in terms of the nitrogen concentration to feed oil in the second-stage reactor during the hydrocracking operation in Example 3. The reaction temperature of the second-stage reactor with which the conversion of fraction of 290°C or higher is 95 vol% was 379°C (2°C higher than in Example 1). The yield of middle distillates (130 to 290°C) was 67%.

#### Example 5

Other than the fact that 10 ppm tert-butyl amine (catalyst deactivation inhibitor) in terms of the nitrogen concentration were mixed with the feed oil in the second-stage reactor, hydrocracking was performed as in Example 4. The temperature of the second-stage reactor at which the conversion of fraction of 290°C or higher is 95 vol% was 390°C. The yield of middle distillates (130 to 290°C) was 67%.

#### Comparative Example

Other than the fact that the gas oil used for pre-sulfiding was changed to gas oil with a nitrogen concentration of 1 ppm, hydrocracking was performed under the same conditions as in Example 1. The concentration of nitrogen adsorbed on the catalyst in second-stage reactor 45 after pre-sulfiding was 0.003% (nitrogen weight/loaded catalyst (fresh catalyst) weight).

The initial deactivation rate when hydrocracking was started as in Example 1 was 2°C/day. It was necessary to keep the temperature of second-stage reactor 45 at 384°C in order to keep the conversion of fractions of 290°C or higher at 95 vol% after the initial deactivation. The yield of middle distillates was 65.4% (middle distillate weight/feed oil weight). When compared to Example 1, it is found that there is little nitrogen treatment

of the catalyst, the initial deactivation speed is high, activity after initial deactivation is over is low, and the middle distillate yield is low.

#### INDUSTRIAL APPLICABILITY

As previously described, according to the invention, hydrocracking catalyst was poisoned by an organic nitrogen compound with a boiling point that is lower than the 50% distillation temperature of the feed oil and that is 200°C or higher, or by the nitrogen compound contained in petroleum fractions having a 95% distillation temperature that is lower than the 50% distillation temperature of the feed oil, and as a result, it was possible to slow the initial deactivation rate of the hydrocracking catalyst and improve activity after the initial deactivation, and further, to improve middle distillate yield. As a result, hydrocracking can be efficiently performed for a long period of time.